

DA

P42664 WO Fuma - Tech

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 September 2003 (18.09.2003)

PCT

(10) International Publication Number
WO 03/077340 A2

- (51) International Patent Classification⁷: **H01M 8/00**
- (21) International Application Number: **PCT/EP03/02550**
- (22) International Filing Date: **12 March 2003 (12.03.2003)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
PG 2002 A 000013 13 March 2002 (13.03.2002) IT
- (71) Applicant (for all designated States except US): **FUMA-TECH GMBH [DE/DE]; Am Grubenstollen 11, 66386 St. Ingbert/Saar (DE).**
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **BAUER, Bernd [DE/DE]; Hildenstrasse 10, 71665 Vaihingen an der Enz (DE). ROZIERE, Jacques [FR/FR]; 58 Avenue d'Occitanie, F-34090 Montpellier (FR). JONES, Deborah [FR/FR]; 58 Avenue d'Occitanie, F-34090 Montpellier (FR). ALBERTI, Giulio [IT/IT]; Via Torelli 67, I-06123 Perugia (IT). CASCIOLO, Mario [IT/IT]; Via Cortonese 74/A, I-06123 Perugia (IT). PICA, Monica [IT/IT]; Fraz. Morano Madonnuccia 37/A, I-06123 Gualda Tadino (IT).**
- (74) Agent: **RUFF, WILHELM, BEIER, DAUSTER & PARTNER; Kronenstr. 30, 70174 Stuttgart (DE).**
- (81) Designated States (national): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.**
- (84) Designated States (regional): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).**
- Published:**
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **ION CONDUCTING COMPOSITE MEMBRANE MATERIALS CONTAINING AN OPTIONALLY MODIFIED ZIRCONIUM PHOSPHATE DISPERSED IN A POLYMERIC MATRIX, METHOD FOR PREPARATION OF THE MEMBRANE MATERIAL AND ITS USE**

(57) Abstract: The invention provides composite membrane materials comprising a polymer of the state of art uniformly filled with a zirconium phosphate, preferably α -zirconium phosphate or zirconium phosphate sulfoarylenphosphonate particels. The composite membrane materials are preferably prepared starting from a solution of a polymer of the state of art and from a colloidal dispersion of α -zirconium phosphate or a zirconium phosphate sulfoarylenphosphonate. The colloidal particles are transferred into the solution of the polymer preferably by mixing the dispersion with the solution or by means of phase transfer. The membrane material is preferably obtained by removing the solvent by evaporation or by a suitable non-solvent. Besides the composite membrane materials and the preparation methods, the use of the above membrane materials is claimed as ionomeric membranes with high overall performance in high temperature, especially hydrogen, and in indirect methanol fuel cells and with decreased methanol crossover in direct methanol fuel cells.

WO 03/077340 A2

Description

Ion conducting composite membrane materials containing an optionally
modified zirconium phosphate dispersed in a polymeric matrix, method
5 for preparation of the membrane material and its use

Fuel cells (FC) using a proton conducting polymeric membrane as a
solid electrolyte are today the more suitable ones for electrical vehicles
10 and portable electrical devices. As well known, three main types of fuel
cells (which usually take the name of the fuel they use) are presently the
object of an intense research: fuel cells fed with pure hydrogen
(hydrogen FC), with hydrogen contained in the reforming gas ("indirect"
methanol FC) and with pure methanol gas or an aqueous solution of
15 methanol ("direct" methanol FC). The proton conducting membrane
plays an important role so that, in order to have a good performance,
specific characteristics of the membrane are required for each type of
the said cells. For their high protonic conductivity at low temperature and
excellent chemical stability, perfluorocarboxysulfonic membranes, such
20 as Nafion, are today the most suitable for hydrogen FC. However,
Nafion membranes are very expensive and, furthermore, their efficiency
decreases at temperatures $>70-80^{\circ}\text{C}$, due to the difficulty of maintaining
the whole membrane hydrated at higher temperatures.

25 The said limitation in the working temperature complicates the cooling of
the stacks; furthermore, when Nafion membranes are used in "indirect
methanol FC", the reforming gas has to be accurately purified from the
presence of carbon monoxide. This is because, especially at low
temperatures, CO poisons the anodic catalyser. This occurs even at
30 levels as low as 10 ppm because of the formation of a Pt-CO adduct.
However, since this adduct is thermo labile, working temperatures
around $120-140^{\circ}\text{C}$ should be high enough to prevent its formation, thus

CONFIRMATION COPY

- 2 -

allowing hydrogen produced by reforming of alkanols or hydrocarbons to be used as a fuel. Finally, Nafion membranes exhibit high permeability to methanol; therefore they cannot be used in "direct" methanol FC.

- 5 The problem to obtain polymeric proton conducting membranes combining good mechanical properties with low methanol permeability and/or high proton conductivity above 70-80 °C can be overcome with at least two different strategies: 1) synthesis of new ionomers possessing the desired properties, 2) improvement of properties of ionomers of the
- 10 state of art by adding inorganic particles which are able to reduce the membrane permeability to methanol, owing to their shape and size, and/or to facilitate (or even increase) the ionomer hydration above 80 °C, owing to their hydrophilic character.
- 15 As far as the second strategy is concerned, according to the patent USA 5, 523, 181, an improvement of humidification of perfluorocarboxysulfonic membranes can be obtained by dispersing particles of silica gel in the above membranes. This modification allows the fuel cell to be operated at reduced relative humidity although at
- 20 temperature below 100 °C. Higher working temperatures can be achieved with a suitable thermal treatment of the silica modified membrane according to the patent EP 0 926 754.

- Furthermore, according to the international patent WO96/29752, the
- 25 permeability to methanol is indeed reduced by adding inorganic particles among which, in particular, zirconium phosphate. Relatively to the problem of an excessive methanol permeability, the recent industrial success in the preparation of nanopolymers filled with organophilic clays clearly indicated that the presence of lamellar particles can decrease to
- 30 a great extent the gas permeability of the polymeric matrix. This is a consequence of the fact that, during the extrusion process, the lamellar particles tend to orientate themselves parallel to the membrane surface.

As schematically shown in figure 1, the presence of suitably oriented particles (A) modifies the path of the diffusing molecule (B): the larger the particle surface, the longer the path. It can therefore be expected that the ionomer permeability to methanol decreases when it is filled with lamellar particles, in agreement with the effect experimentally found for zirconium phosphate in the above international patent. However, it can be observed that, in the above patent, the importance of size and orientation of the lamellar particles was not well understood. In addition, since zirconium phosphate is completely insoluble in known solvents, its insertion was carried out by in situ precipitation. This does not allow to control the orientation, the size and the exfoliation of the lamellar particles.

It was therefore recognized the need of inserting zirconium phosphate in ionomeric matrices by using a completely different procedure which makes it possible to obtain uniform dispersions of lamellar particles having desired size and oriented prevalently parallel to the membrane faces. However, since zirconium phosphate has a relatively low proton conductivity, its dispersion in an ionomer of high proton conductivity may be associated with a decrease of the overall conductivity, especially for high loadings of inorganic particles.

In order not to decrease, and possibly to increase the ionomer conductivity, there is the need of modifying the proton conducting membranes of the state of art by dispersing, in the polymeric matrix, lamellar hydrophilic components exhibiting proton conductivity comparable with, or higher than, the conductivity of the ionomer where they have to be dispersed. Since lamellar compounds with high proton conductivity are very insoluble, in this case too it was recognized the need of finding a procedure, different from the in situ precipitation, suitable to disperse uniformly and with the right orientation lamellar particles in the polymeric matrix.

It is known from the literature (G. Alberti, M. Casciola, U. Costantino, A. Peraio, E. Montoneri, Solid State Ionics 50 (1992) 315; G. Alberti, L. Boccali, M. Casciola, L. Massinelli, E. Montoneri, Solid State Ionics 84 (1996) 97) that some α - or γ -layered zirconium phosphate sulfoarylenphosphonates exhibit proton conductivity up about 0.1 S cm^{-1} . These compounds are represented by the general formulae $\text{Zr}(\text{O}_3\text{POH})_{2-x}(\text{O}_3\text{P-Ar})_x \cdot n\text{H}_2\text{O}$, with $0 < x \leq 2$ (α -type compounds), or $\text{Zr}(\text{PO}_4)(\text{O}_2\text{P}(\text{OH})_2)_{1-x}(\text{HO}_3\text{P-Ar})_x \cdot n\text{H}_2\text{O}$, with $0 < x \leq 1$ (γ -type compounds), where Ar is an arylensulfonated group. The inventors have recognised that these compounds must be considered more hydrophilic than silica due to the super acidic character of the sulfonic function.

Powders of amorphous zirconium phosphate metasulfophenylenphosphonates of composition $\text{Zr}(\text{O}_3\text{POH})_{2-x}(\text{O}_3\text{P-Ar})_x \cdot n\text{H}_2\text{O}$, with $x=1$ and 1.5, supported by sulfonated poly-ether-ether-ketone were already used for the preparation of composite membranes containing 40 % proton conductor without any loss of the ionomer conductivity (E. Bonnet, D.J. Jones, J. Rozière, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, B. Bauer, A. Peraio, E. Ramunni, J. New Mat. Electrochem. Systems, 3 (2000) 87). Similar results were also obtained for Nafion 1100 membranes loaded with powder of an α -titanium phosphate metasulfophenylenphosphonate up to 20 % (G. Alberti, U. Costantino, M. Casciola, S. Ferroni, L. Massinelli, P. Staiti, Solid State Ionics 145 (2001) 249).

It was now surprisingly found that both amorphous and α - or γ -layered zirconium phosphate as well as zirconium phosphate metasulfoarylenphosphonates form stable colloidal dispersions in some organic solvents (e.g. N, N'-dimethylformamide (DMF), N-methyl-2-

pyrrolidone (NMP), dimethylsulfoxide, acetonitrile, alkanols) or in their mixtures with water.

It was also surprisingly found that α -zirconium phosphate $Zr(O_3POH)_2$,
5 after a suitable process of intercalation-deintercalation of propylamine, can be dispersed in dimethylformamide or N-methylpyrrolidone. Moreover, depending on the crystallinity degree of the starting material and on the conditions used in the deintercalation process, it is possible to obtain dispersions of lamellar particles with thickness ranging from ca.
10 5 to ca. 100 nm, preferably 5-10 nm, and surface area from ca. 0.1 to ca. 10 μm^2 , especially 0,2-1 μm^2 .

The availability of the above colloidal dispersions is a good starting point to disperse uniformly α -zirconium phosphate or zirconium phosphate-sulfoarylenphosphonates into a polymeric matrix. In addition, since the
15 size of the lamellar particles in these dispersions depends to a great extent on the size of the particles of the starting material, it is possible to fill the polymeric matrix with lamellar particles of controlled size and shape. As mentioned above, this is a clear advantage in comparison
20 with the in situ formation of α -zirconium phosphate reported in the already cited international patent WO96/7952 and appears to be particularly important in order to control the reduction of membrane permeability to the fuel and specifically to methanol.

25 It is an object of the present invention to provide a composite membrane material made of an ionomer of the state of art and of a layered zirconium phosphate sulfoarylenphosphonate exhibiting proton conductivity comparable with, or possibly higher than, the conductivity of the pure ionomeric membrane material. The conductivity of the
30 zirconium phosphate containing membrane material is $> 5 \times 10^{-4} S cm^{-1}$ at temperatures of 0 °C to 200 °C. In one embodiment conductivity of a

- 6 -

modified zirconium phosphate, especially zirconium phosphate sulfoarylenphosphonate, containing membrane material is $>10^{-2} \text{ S cm}^{-1}$ at 70 °C and 95 % relative humidity.

- 5 It is a further object of the present invention to provide a composite membrane material made of an ionomer of the state of art filled with well-dispersed lamellar particles of α -zirconium phosphate of controlled thickness and surface.
- 10 It is a further object of the present invention to provide a procedure for the preparation of a composite membrane material made of the said ionomer and of a zirconium phosphate, preferably a layered zirconium phosphate, especially α -zirconium phosphate, or of a zirconium phosphate sulfoarylenphosphonate, starting from a solution of the
- 15 ionomer and from a colloidal dispersion of α -zirconium phosphate or of the said zirconium phosphate sulfoarylenphosphonate.

- The invention concerns in one aspect the preparation of a colloidal dispersion of α -zirconium phosphate or of a proton conducting zirconium
- 20 phosphate sulfoarylenphosphonate in a suitable solvent or mixture of solvents, and in the subsequent transfer of the colloidal particles into a solution of a polymer, especially an ionomer, of the state of art. The mixture thus obtained is cast on the surface of a smooth plane support and the solvent is removed by heating or by using a suitable non-
- 25 solvent. Transfer of the colloidal particles into the polymer, especially ionomer, solution can be carried out (1) by mixing the polymer, especially the ionomer, solution with the colloidal dispersion or (2) by means of "phase transfer". It is possible to use noncharged polymers as conductivity is contributed by the zirconium phosphate. Preferably there
- 30 are used ionomers, especially sulfonated polymers due to their conductivity at low temperatures ($<100 \text{ °C}$). There can be used

- 7 -

perfluorosulfonic polymers, especially Nafion, Hyflon or Sterion, sulfonated polyvinylidenefluoride, sulfonated polyetherketones, especially sPEK, sPEEK, sPEKK, sPPEK, sPEEKK or sPEKEKK, sulfonated polybenzimidazoles, sulfonated polysulfones sulfonated
5 polyphenylsulfones and sulfonated polyethersulfones. In case (1) the same solvent can be used for the solution and the dispersion. Alternatively, if different solvents are used for the solution and the dispersion, it must be avoided that the solvent of the polymer may provoke colloid flocculation and the solvent of the colloidal dispersion
10 may cause polymer precipitation.

The overall content of zirconium phosphate in the membrane material is 0,5 % - 70 %, preferably 5 % - 40 %, especially 10 % - 25 % by weight. For the use as direct methanol fuel cells content of zirconium phosphate
15 is about 10 wt % - 20 wt %, especially 12 wt % to 15 wt %, were as for high temperature fuel cells, especially hydrogen fuel cells, a zirconium phosphate of up to 30 wt %, preferably up to 25 wt %, is used.

For direct methanol fuel cells there is employed a mixture of large and
20 small dies, whereas the large dies prevent from methanol permeating the membrane and the small dies prevent from reagglomeration of the large dies. For high temperature fuel cells, especially hydrogen fuel cells, there are employed solely small dies.

The diameter of the large dies is in the range from 0,1 to 1 μm whereas
25 the diameter of the small dies is about 10-50 nm.

For medium temperature fuel cells dispersed, amorphous as well as semi-crystalline zirconium phosphate is applied. The diameter ranges from 10-50 nm.

30 Semi-crystalline zirconium phosphate material enhances mechanical stability and limits swelling in x- and y-plane. Diameter can be up to 100-500 nm.

L

- 8 -

Crystalline zirconium phosphate material is suitable for direct methanol fuel cells with diameters of 1-10 μm .

5 The thickness of the zirconium phosphate and zirconium phosphate sulfoarylenphosphonate dies ranges in the scale of single molecule layers. The overall thickness of the composite membranes is between 10 μm and 100 μm , preferably 30-60 μm .

10 An object of the invention are preferably also membranes comprising the composite membrane material for fuel cells or in fuel cells.

Another object of the invention are further fuel cells comprising the composite membrane material.

15 The following examples have the purpose of facilitating the understanding of the invention, and do not intend to limit in any manner its scope, which is solely defined by the appended claims.

20 Figure 1 shows the orientation of particles in the composite membrane material

Figure 2 shows conductivity behaviour of PFSA + 3 % ZrP

Figure 3 shows conductivity of PPEK + 20 % ZrP

Figure 4 shows polarisation curve of s-PEEK + 20 % ZrP compared to Nafion 117

25 Figure 5 shows conductivity behaviour of PFS-Li + 10 % ZrSPP

Figure 6 shows an 20.000x magnification of s-PEK + 20% Zr(SPP)_{1.3}

Figure 7 shows an 10.000x magnification of s-PEK + 10% Zr(SPP)_{1.3}

Figure 8 shows conductivity of s-PEK + 20 % ZrSPP

Figure 9 shows conductivity of s-PEKK + 20 % ZrSPP

30

EXAMPLES

EXAMPLE 1

Preparation of a composite membrane material made of sulfonated
5 polyetherketone / α -zirconium phosphate by mixing the ionomer solution
in NMP with a colloidal dispersion of α - zirconium phosphate in DMF

a) A colloidal dispersion of α -zirconium phosphate intercalated with
propylamine ($\text{Zr}(\text{O}_3\text{POH})_2 \cdot \text{C}_3\text{H}_7\text{NH}_2$) in water is prepared according to G.
10 Alberti, M. Casciola and U: Costantino, J. Colloid and Interface Science
107 (1985) 256. The dispersion is treated with 1M HCl so that $\text{pH} < 2$.
The solid is separated from the solution and washed with
dimethylformamide under vigorous stirring. A gelatinous precipitate,
containing 4 % anhydrous α -zirconium phosphate, settles by
15 centrifugation at 3000 rpm. Washing is repeated up to elimination of
chloride ions.

b) A weighed amount of sulfonated polyetherketone with ion exchange
capacity 1.3 meg/g (s-PEK1.3), corresponding to 9 g of anhydrous
20 ionomer, is dissolved in NMP under nitrogen atmosphere at 130 °C. 25 g
of the above gelatinous precipitate of α -zirconium phosphate are
dispersed into the polymer solution. This mixture is used to prepare a
membrane material by means of an Erichsen semi/automatic film casting
processor. The solvent is removed by heating 1 hour at 80 °C and
25 30 minutes at 120 °C. The membrane material thus obtained (thickness
0.035 mm, 10 % inorganic particles) is kept in water.

EXAMPLE 2

30 Preparation of a composite membrane material made of
s-PEK/zirconium phosphate sulfophenylphosphonate by mixing the

ionomer solution in DMF with a colloidal dispersion of the zirconium phosphate sulfophenylenphosphonate in the same solvent.

a) Preparation of $\text{Zr}(\text{O}_3\text{POH})_{0.6}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.4}$

- 5 7.5 ml of 1M H_3PO_4 and 15 ml of 1M metasulfophenylenphosphonic acid are mixed and concentrated by heating overnight at 80 °C. The dense solution thus obtained is mixed with 50 ml of acetonitrile and water is added until a clear solution is obtained. 13.6 ml of an aqueous solution of 0.75M ZrOCl_2 are then added drop wise to the acetonitrile solution.
- 10 The white precipitate thus formed is held under vigorous stirring for half an hour and washed two times with 2M HCl (2 x 50 ml) and two times with acetonitrile (2 x 50 ml). The slurry, obtained after centrifugation at 3000 rpm, is used for the preparation of a colloidal dispersion in DMF.

- 15 b) Preparation of a colloidal dispersion of $\text{Zr}(\text{O}_3\text{POH})_{0.6}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.4}$ in DMF

- A weighed amount of the above slurry is mixed with an equal amount of DMF and stirred overnight. The mixture is left at rest for one day to allow sedimentation of the solid. The supernatant colloidal dispersion contains
- 20 9 % $\text{Zr}(\text{O}_3\text{POH})_{0.6}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.4}$, 50 % DMF and 41 % acetonitrile.

c) Membrane material preparation

- A weighed amount of s-PEK1.3 (corresponding to 1.2 g of anhydrous ionomer) is dissolved under vigorous stirring in 8 g of NMP at 130 °C.
- 25 Subsequently, 3.37 g of the colloidal dispersion described in b) are mixed with 9.05 g of the s-PEK1.3 solution. This mixture is held under stirring for half an hour and then cast on a glass plate. The solvent is evaporated as indicated in example 1. The membrane material thus obtained (thickness 0.05 mm, 20 % of inorganic material) is kept in
- 30 water.

The membrane material conductivity at 100 °C is $1.2 \cdot 10^{-3} \text{ S cm}^{-1}$ and $1.3 \cdot 10^{-2} \text{ S cm}^{-1}$ at 80 % and 100 % relative humidity, respectively.

COMPARATIVE EXAMPLE 2

- 5 The polymer solution used in example 1 is cast on a glass plate. The film thus obtained is heated one hour at 80 °C and half an hour at 120 °C. The resulting membrane material is detached by immersing the glass plate in water. The membrane material conductivity at 100 °C is $1.1 \cdot 10^{-3} \text{ S cm}^{-1}$ and $1.1 \cdot 10^{-2} \text{ S cm}^{-1}$ at 80 % and 100 % relative humidity,
10 respectively.

EXAMPLE 3

- Preparation, by phase transfer, of a membrane material of amorphous
15 zirconium phosphate sulfophenylenphosphonate dispersed in sulfonated polyetherketone.

- The gelatinous precipitate of example 1a is first heated at 80 °C and then at 120 °C to remove acetonitrile. An aqueous dispersion of 20 %
20 anhydrous zirconium phosphate sulfophenylenphosphonate is held under stirring for 1 hour, and then left at rest for two hours to allow sedimentation of the largest particles. The liquid phase is decanted off. This phase contains 15 % $\text{Zr}(\text{O}_3\text{POH})_{0.6}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.4}$. An amount of 1.05 g of s-PEK1.3 is dissolved under vigorous stirring in 8 g of an
25 appropriate solvent, for example, NMP, DMF or dimethylsulfoxide, at 130 °C. The above aqueous dispersion is mixed with the polymer solution so that the weight percent of inorganic material in dry membrane material is in the range 1 – 40 %, preferably 5 – 30 %. The lower boiling solvent is removed by evaporation and the inorganic
30 material passes from the aqueous to the organic phase. The single

phase product obtained is cast on a glass support and the resulting film dried as described in example 1.

The conductivity of a membrane material containing 10 % of inorganic material at 100 °C and 80 % relative humidity is $1.3 \cdot 10^{-3} \text{ S cm}^{-1}$.

5

EXAMPLE 4

Preparation of a perfluorosulfonic acid (PFSA) hybrid membrane for medium temperature fuel cells containing 3 wt. % of amorphous α -zirconium phosphate (ZrP)

10

29,12 g of a 10 wt.% solution of the Li-form of the perfluorosulfonic acid polymer PFSA (Nafion®, EW 1150) in N-methyl-2 pyrrolidone (NMP) and 1,2 g of a 10 wt.% gel of amorphous exfoliated ZrP in NMP/H₂O are mixed by carefully adding the colloidal dispersion of exfoliated ZrP in small quantities under vigorous stirring into the PFS-Li solution. After filtration of the mixture through a 10 μm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 μm , feed rate: 10mm/s).

15

After applying following drying protocol and delamination from the glass plate, a film of 50-60 μm thickness is obtained.

20

Drying protocol: 30 min at 50 °C, then 30 min at 60 °C, then 30 min 80 °C, then 30 min 120 °C

Before further characterisation, the film was carefully conditioned in 1M H₂SO₄, then repeatedly washed in demineralised water until neutral pH was obtained.

25

The following conductivity behaviour (figure 2) was obtained in a temperature controlled measuring cell under full humidification.

30

EXAMPLE 5

Preparation of a copolyetherketone hybrid membrane for direct methanol fuel cells containing 20 wt. % of semi crystalline α -zirconium phosphate (ZrP)

5

19,45 g of a 15 wt.% solution of the polyphthalazinoneetherketone polymer (PPEK) (EW 900) in NMP and 5,72 g of a 14 wt.-% gel of semi crystalline exfoliated ZrP in DMF/H₂O is mixed by carefully adding the ZrP-gel in small quantities under vigorous stirring into the PPEK solution.

- 10 After filtration of the mixture through a 40 μ m filter, a film is prepared on a glass plate using a doctor blade (gap: 600 μ m, feed rate: 10 mm/s).

After applying following drying protocol and delamination from the glass plate, a film of 50-60 μ m thickness is obtained.

- 15 Drying protocol: 30 min at 80 °C, then 60 min 120 °C

Before further characterisation, the film was delaminated in demineralised water.

- 20 The following conductivity (figure 3) is measured in a conductivity cell in 0,5 Mol NaCl and the flux of methanol in a diffusion cell applying a feed concentration of 5Mol/l CH₃OH versus demineralised water at 50 °C.

EXAMPLE 6

- 25 Preparation of a polyetheretherketone (PEEK) hybrid membrane for direct methanol fuel cells containing 20 wt. % of crystalline α -zirconium phosphate (ZrP)

- 30 29,12 g of a 10 wt.% in DMSO solution of the H-form of a sulfonated Victrex PEEK polymer (EW 735) and 7,3 g of a 10 wt.-% gel of crystalline ZrP in DMF/H₂O is mixed by carefully adding the ZrP-gel in

small quantities under vigorous stirring into the s-PEEK solution. After filtration of the mixture through a 40 μm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 μm , feed rate: 10 mm/s).

- 5 After applying following drying protocol and delamination from the glass plate, a film of 50-60 μm thickness is obtained.

Drying protocol: 30 min at 60 °C, then 30 min at 80 °C, then 30 min 80 °C, then 30 min 120 °C

Before further characterisation, the film was carefully conditioned in

- 10 1M H_2SO_4 , then repeatedly washed in demineralised water until neutral pH was obtained.

The following polarisation curve (figure 4) was obtained compared to a Nafion117 film from Dupont, in a single cell (20 cm^2) at 80 °C under

- 15 DMFC (direct methanol fuel cell)-conditions: Anode 1 Mol/l methanol in water. Cathode O_2 . Electrodes: Anode: 2,4 mg/cm^2 Pt/Ru; Cathode: 3 mg/cm^2 Pt.

20 EXAMPLE 7

Preparation of a perfluorosulfonic acid (PFSA) hybrid membrane for medium temperature fuel cells containing 10 wt. % of zirconium phosphate sulfophenylenphosphonate (ZrSPP)

- 25 1g ZrSPP is solubilised in 10 ml H_2O . 20 ml NMP is added and the mixture is reduced in volume to 61 % at 80 °C. A clear solution is obtained. 25 g of a 10 wt.% in NMP solution of the Li-form of the perfluorosulfonic acid polymer PFSA (Nafion®, EW 1150) and 6 g of the afore mentioned ZrSPP solution is mixed by carefully adding the ZrSPP-
- 30 solution in small quantities under vigorous stirring. After filtration of the mixture through a 40 μm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 μm , feed rate: 10 mm/s).

After applying following drying protocol and delamination from the glass plate, a film of 50-60 μm thickness is obtained.

Drying protocol: 30 min at 50 °C, then 30 min at 60 °C, then 30 min
5 80 °C, then 30 min 120 °C

Before further characterisation, the film was carefully conditioned in 1M H_2SO_4 , then repeatedly washed in demineralised water until neutral pH was obtained.

10 The following conductivity behaviour (figure 5) was obtained in a temperature controlled measuring cell under full humidification.

EXAMPLE 8

15 Preparation of a polyetherketone (PEK) hybrid membrane for medium temperature fuel cells containing 10%wt. of zirconium phosphate sulfophenylenphosphonate (ZrSPP)

1g of ZrSPP is solubilised in 10 ml H_2O . 20 ml NMP is added and the
20 mixture is reduced in volume to 61 % at 80 °C. A clear solution of 5 wt. % is obtained. 29,12 g of a 10 wt.-% in NMP solution of the H-form of a sulfonated PEK polymer (equivalent weight: 735 g/equivalent) and 14,6 g of the afore mentioned ZrSPP solution is mixed by carefully adding the ZrSPP-solution in small quantities under vigorous stirring into
25 the s-PEKK solution.

After filtration of the mixture through a 40 μm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 μm , feed rate: 10mm/s).

After applying following drying protocol and delamination from the glass
30 plate, a film of 50-60 μm thickness is obtained.

Drying protocol: 30 min at 60 °C, then 30 min at 80 °C, then 30 min
80 °C, then 30 min 120 °C

- 16 -

Before further characterisation, the film was carefully conditioned in 1M H₂SO₄, then repeatedly washed in demineralised water until neutral pH was obtained.

- 5 The following conductivity (figure 8) was obtained at reduced humidity (90 %). The reference measurement is given as s-PEK.

EXAMPLE 9

- 10 Preparation of a sulfonated polyetherketoneketone (s-PEKK) hybrid membrane for direct methanol fuel cells containing 20 wt. % of crystalline zirconium phosphate sulfophenylphosphonate (ZrSPP)

- 30,22 g of a 10 wt. % in NMP solution of the polyetherketoneketone (PEKK) polymer (equivalent weight: 775 g/equivalent) and 10,78 g of a 15 7 wt. % gel of amorphous exfoliated ZrSPP in DMF/ H₂O is mixed by carefully adding the ZrSPP-gel in small quantities under vigorous stirring into the PEKK solution.

- After filtration of the mixture through a 40 µm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 µm, feed rate: 10mm/s). 20

After applying following drying protocol and delamination from the glass plate, a film of 50-60 µm thickness is obtained.

- Drying protocol: 30 min at 60 °C, 30 min at 80 °C, then 60 min 120 °C 25

- The following conductivity (figure 9) was obtained in 0,5 Mol NaCl and flux of methanol was measured in a diffusion cell applying a feed concentration of 5 Mol/l CH₃OH versus demineralised water at 50 °C. 30

Patent claims

1. An ion conducting composite membrane material consisting of a polymeric matrix filled with particles of cation, particularly proton,
5 conducting, optionally modified, zirconium phosphate.
2. The membrane material according to claim 1 or 2 wherein the zirconium phosphate is a zirconium phosphate of the general formula $\text{Zr}(\text{O}_3\text{POH})_{2-x}(\text{O}_3\text{P-Ar})_x$, where Ar is a sulfoarylen group and $0 \leq x$.
10
3. The membrane material according to claim 1 or 2 wherein the zirconium phosphate is α -zirconium phosphate $\text{Zr}(\text{O}_3\text{POH})_2$.
4. The membrane material according to claim 1 wherein the modified
15 zirconium phosphate is a zirconium phosphate sulfoarylenphosphonate $\text{Zr}(\text{O}_3\text{POH})_{2-x}(\text{O}_3\text{P-Ar})_x$ wherein Ar is a sulfoarylen group and $0 < x \leq 2$.
5. The membrane material according to one of the claims 1-4 wherein the conductivity of the membrane material containing optionally modified
20 zirconium phosphate is $> 5 \times 10^{-4} \text{ S cm}^{-1}$ at temperatures of 0°C to 200°C and a relative humidity of 100 %.
6. The membrane material according to one of the claims 1-5, wherein the conductivity of the membrane material containing zirconium
25 phosphate, preferably a modified zirconium phosphate, especially zirconium phosphate sulfoarylenphosphonate, is $> 10^{-2} \text{ S cm}^{-1}$ at 70°C and 95 % relative humidity.
7. The membrane material according to claim 1 wherein the polymeric
30 matrix of the membrane material is that of an ionomer, especially of a proton conducting ionomer.

8. The membrane material according to one of the preceding claims wherein the polymeric matrix of the membrane material is at least one synthetic ionomer of the group consisting of perfluorosulfonic polymers, sulfonated polyvinylidenefluoride, sulfonated polyetherketones, polybenzimidazoles, sulfonated polyphenylsulfones, sulfonated polysulfones and sulfonated polyethersulfones.

9. The membrane material according to one of the claims 2 and 4-8 wherein the zirconium phosphate sulfoarylenphosphonate contains specifically one or more phosphonate groups bonded to the zirconium atom.

10. The membrane material according to one of the claims 2 and 4-9 wherein the sulfoarylenphosphonate group is meta-sulfophenylene phosphonate.

11. The membrane material according to one of the preceding claims wherein optionally modified zirconium phosphate is of layered type.

12. The membrane material according to one of the preceding claims wherein the amount of optionally modified zirconium phosphate in the membrane material is 0,5 % – 70 %, preferably 5 % - 40 %, especially 10 % - 25 % by weight.

13. A method for the preparation of the proton conducting composite membrane material according to one of claims 1-12 based on the following steps:

a) preparation of a layered zirconium phosphate or modified zirconium phosphate,

- 19 -

- b) preparation of a colloidal dispersion of the zirconium phosphate or modified zirconium phosphate in a suitable solvent or mixture of solvents,
- c) transfer of the zirconium phosphate or modified zirconium phosphate particles from the said colloidal dispersion to a solution of a polymer,
- d) forming membrane materials by using the mixture and eliminating the solvent.

14. The method for the preparation of the proton conducting composite membrane material according to claim 13 wherein the polymer is the ionomer of claim 7 or 8.

15. A method for the preparation of a proton conducting composite membrane material consisting of a synthetic ionomer of claims 7 or 8 filled with lamellar particles of α -zirconium phosphate based on the following steps:

- a) exfoliation of α -zirconium phosphate in aqueous solution by intercalation - deintercalation of an alkyl amine,
- b) dispersion of α -zirconium phosphate, obtained from the previous intercalation deintercalation process, into an organic solvent,
- c) transfer of the exfoliated zirconium phosphate particles from the said colloidal dispersion to a solution of a polymer,
- d) forming membrane materials by using the mixture and eliminating the solvent.

16. The methods for the preparation of the proton conducting composite membrane materials according to one of claims 13-15 wherein the mixture containing the polymer and the α -zirconium

- 20 -

phosphate or modified zirconium phosphate is obtained by mixing the ionomer solution with the colloidal dispersion of the layered α -zirconium phosphate or zirconium phosphate sulfoarylenphosphonate.

5 17. The method for the preparation of the proton conducting composite membrane material according to one of claims 13-16 wherein the colloidal dispersion of the α -zirconium phosphate or modified zirconium phosphate is obtained by using organic solvents selected from N, N'-dimethylformamide, N-methyl-2-pyrrolidone, dimethylsulfoxide,
10 acetonitrile and alkanols, preferably N, N'-dimethylformamide and/or N-methyl-2-pyrrolidone, or their mixtures or water or mixtures of water and organic solvent.

15 18. The methods for the preparation of the proton conducting composite membrane materials of one of claims 13-17 wherein the ionomer solution and the colloidal dispersion are prepared in the same solvent or in different solvents, provided that the mixing of the solution with the dispersion does not cause colloid flocculation or ionomer precipitation.

20 19. The method for the preparation of the proton conducting composite membrane material according to claims 13-18 wherein the mixture containing the ionomer and the layered α -zirconium phosphate or zirconium phosphate sulfoarylenphosphonate is obtained by "phase
25 transfer".

20. The methods for the preparation of the proton conducting composite membrane materials according to claims 13-18 wherein the solvent is removed from the polymer-colloid mixture by evaporation.

30

- 21 -

21. The methods for the preparation of the proton conducting composite membrane materials according to claims 13-18 wherein the solvent is removed from the polymer-colloid mixture by the use of a non-solvent, preferably water.

5

22. Use of the composite membrane materials of one of claims 1-12 as ionomeric membrane materials with high mechanical properties and/or decreasing methanol permeability.

10 23. Use of the composite membrane materials of one of claims 1-12 as ionomeric membrane materials with high overall performance in hydrogen, in indirect and in direct methanol fuel cells.

24. Use of the composite membrane materials containing α -zirconium phosphate according to one of claims 1-12 as ionomeric membrane materials with high overall performance in hydrogen and in indirect methanol fuel cells operating preferably at temperatures $>80^{\circ}\text{C}$.

15 25. Use of the composite membrane material according to one of claims 1-12 in direct methanol fuel cells.

20

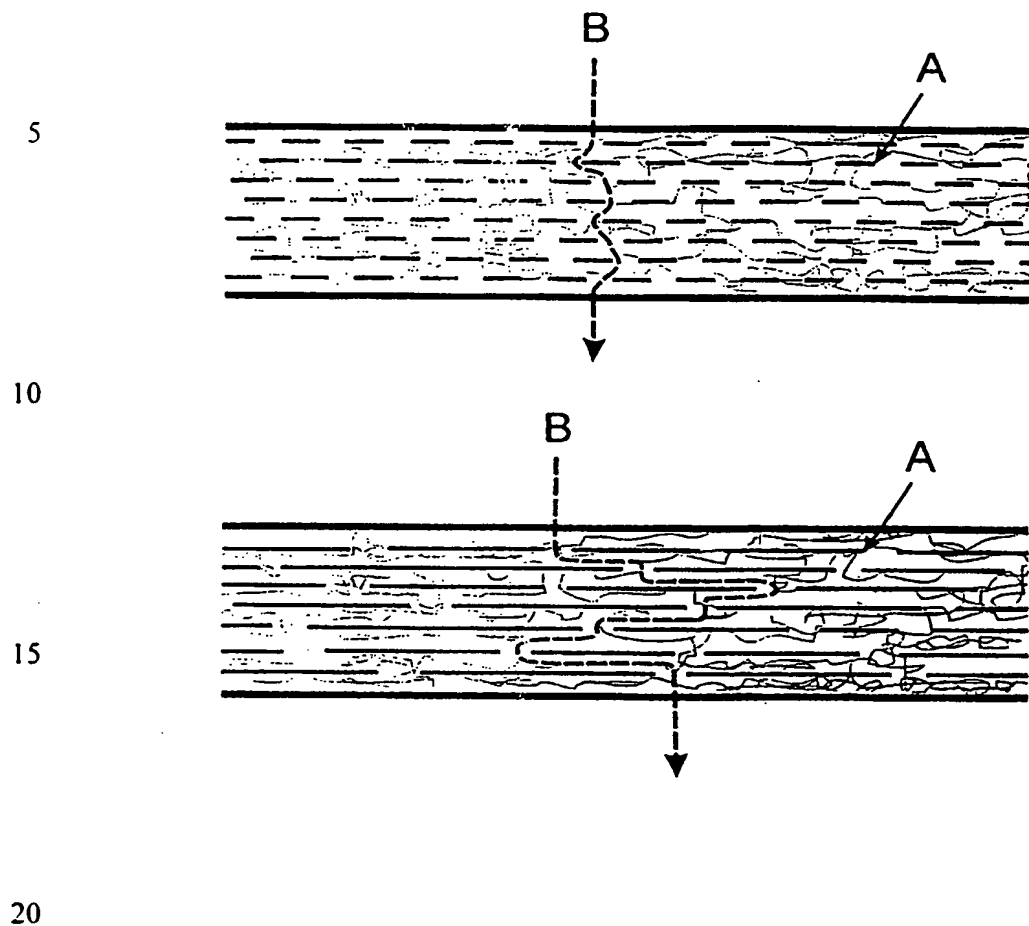
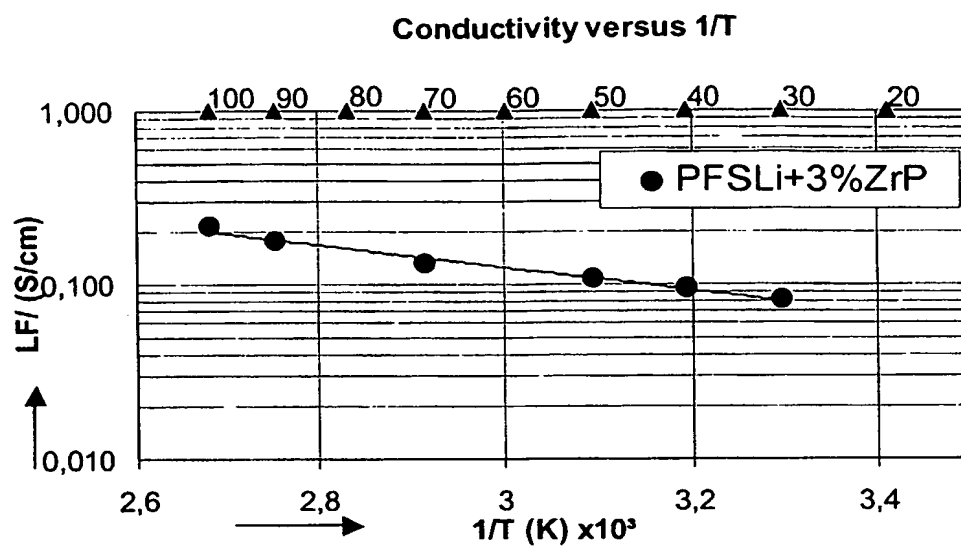
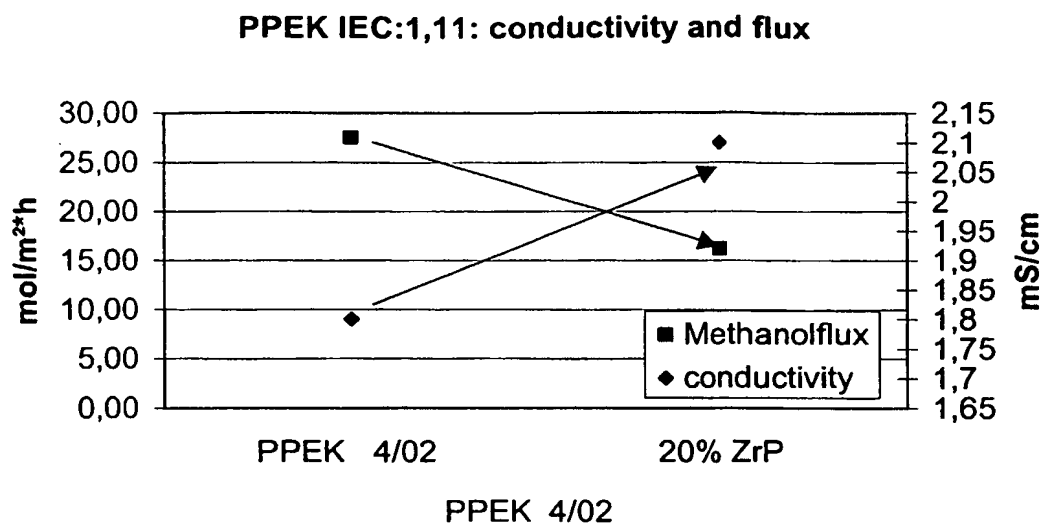


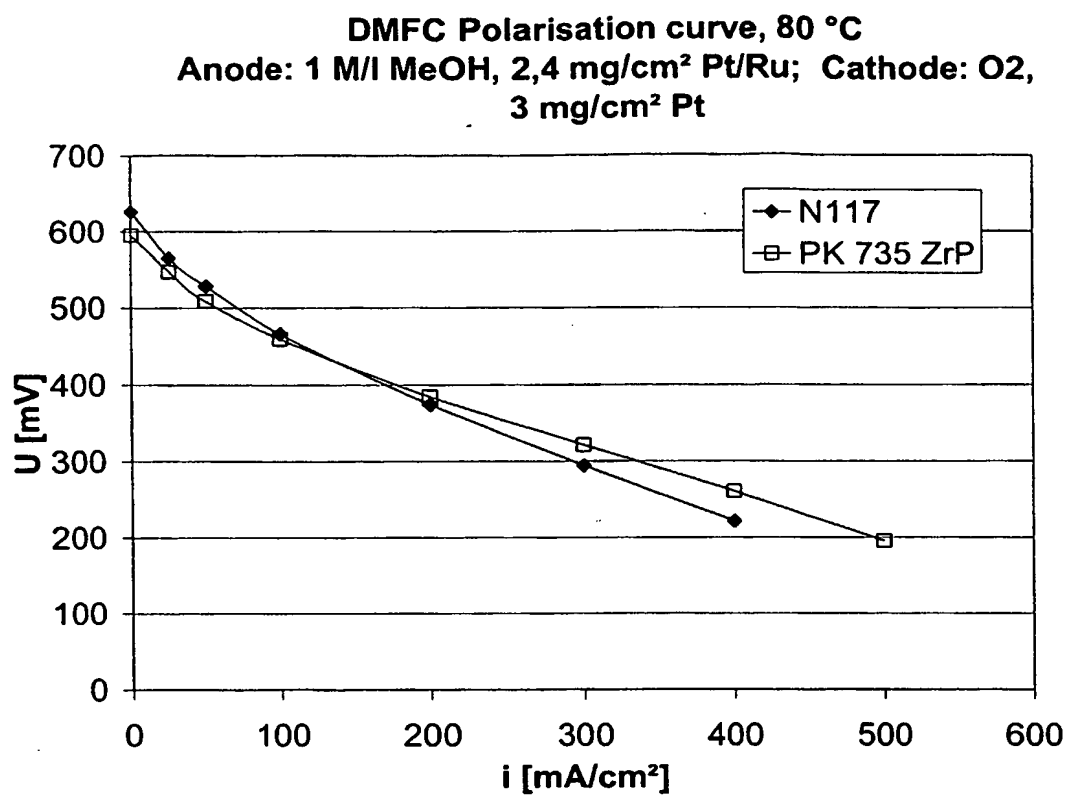
Figure 1



5 Figure 2



5 Figure 3



5 Figure 4

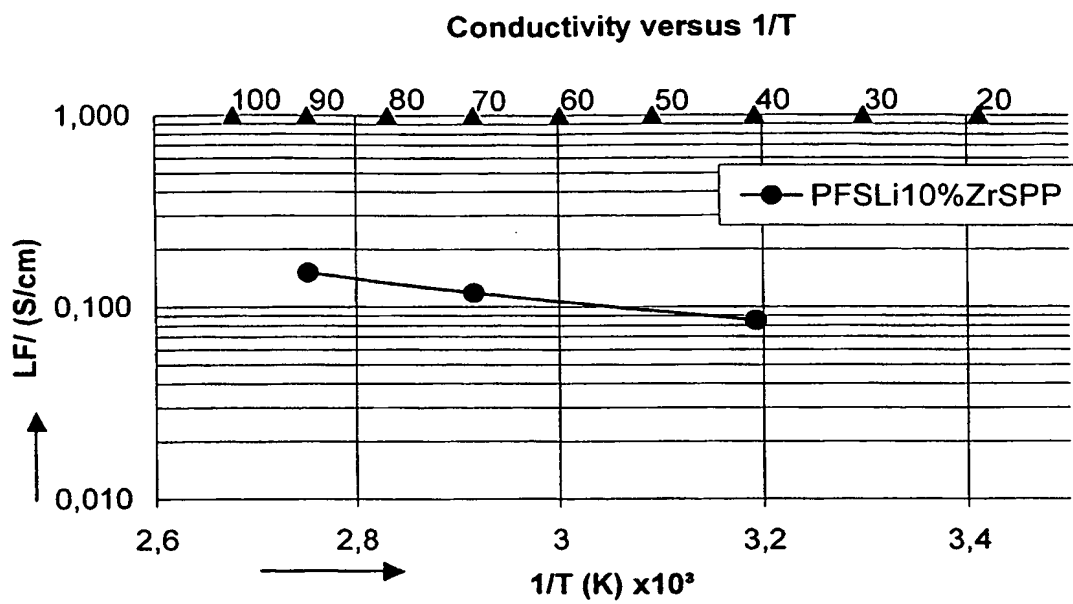


Figure 5

BEST AVAILABLE COPY

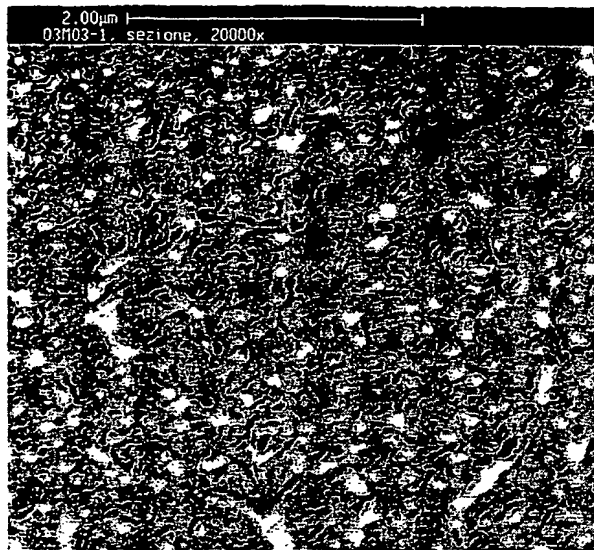
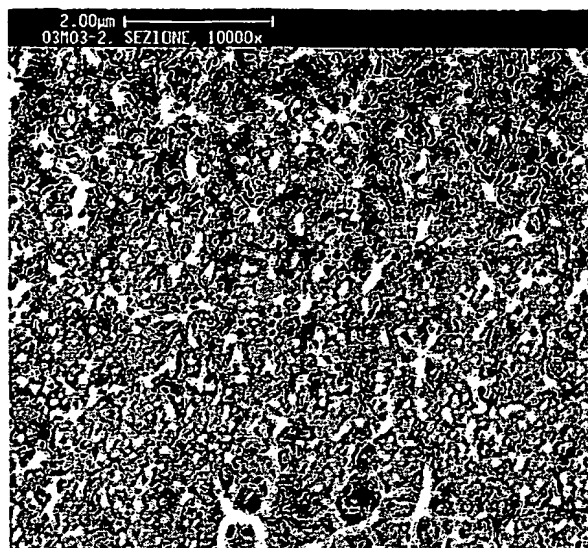


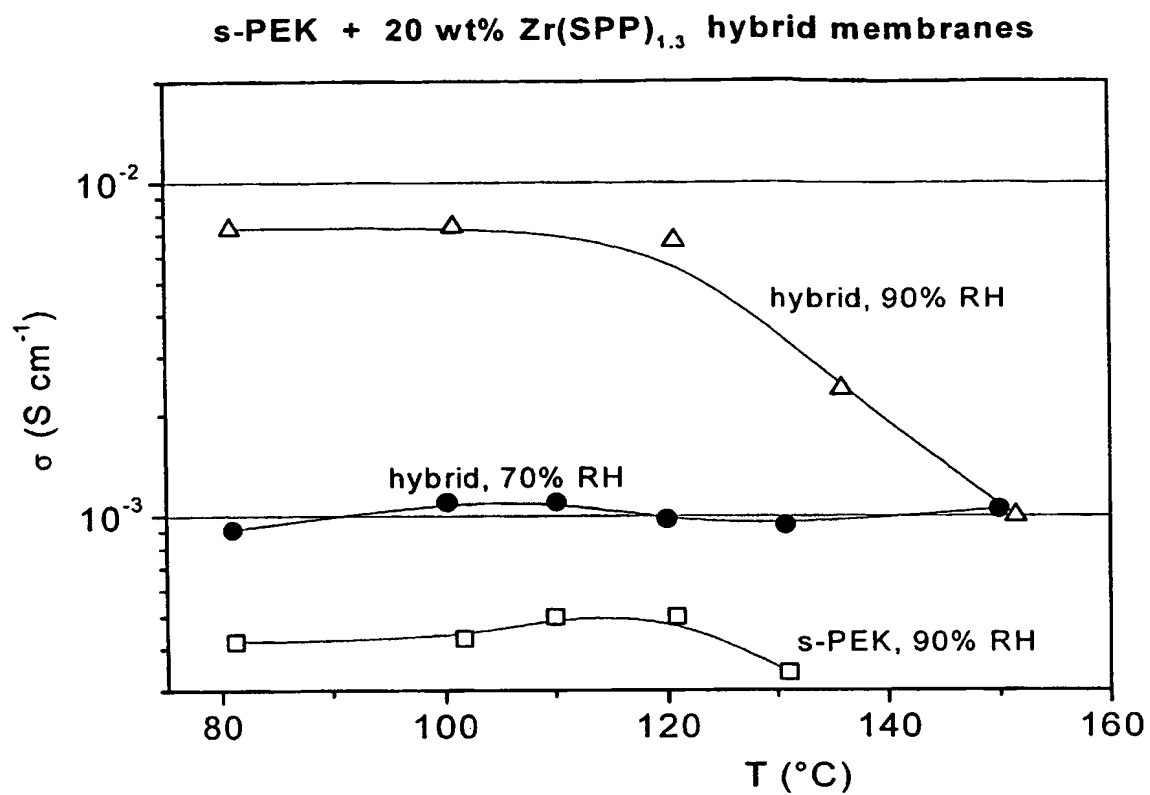
Figure 6

5

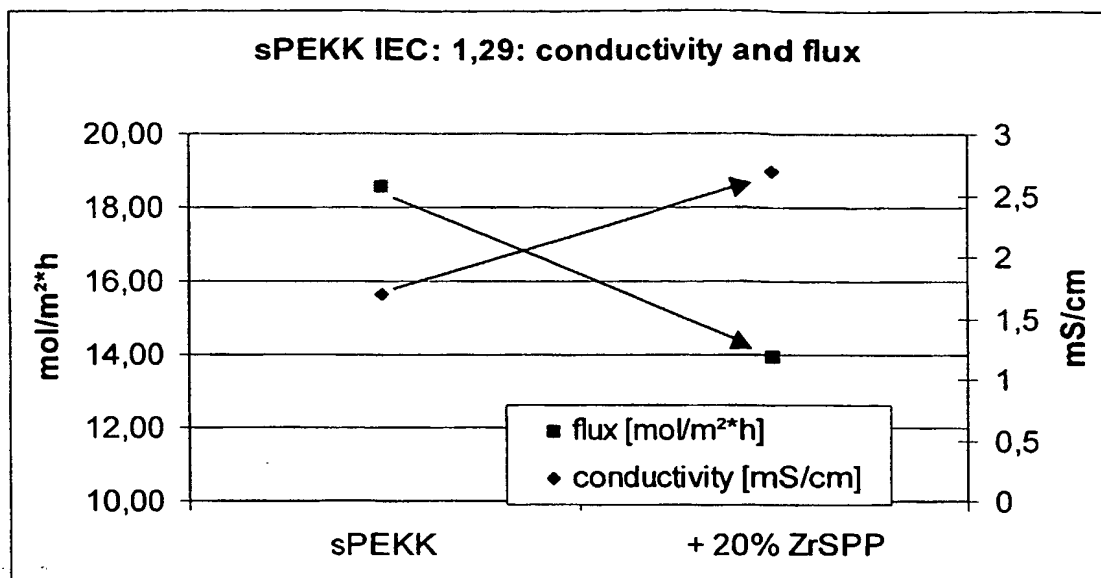
BEST AVAILABLE COPY



5 Figure 7



5 Figure 8



5 Figure 9

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
18 September 2003 (18.09.2003)

PCT

(10) International Publication Number
WO 2003/077340 A3

- (51) International Patent Classification⁷: **H01M 8/10**, 8/02, 2/16
- (21) International Application Number: **PCT/EP2003/002550**
- (22) International Filing Date: 12 March 2003 (12.03.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
PG 2002 A 000013 13 March 2002 (13.03.2002) IT
- (71) Applicant (for all designated States except US): **FUMA-TECH GMBH** [DE/DE]; Am Grubenstollen 11, 66386 St. Ingbert/Saar (DE).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **BAUER, Bernd** [DE/DE]; Hildenstrasse 10, 71665 Vaihingen an der Enz (DE). **ROZIERE, Jacques** [FR/FR]; 58 Avenue d'Occitanie, F-34090 Montpellier (FR). **JONES, Deborah** [FR/FR]; 58 Avenue d'Occitanie, F-34090 Montpellier (FR). **ALBERTI, Giulio** [IT/IT]; Via Torelli 67, I-06123 Perugia (IT). **CASCIOLA, Mario** [IT/IT]; Via Cortonese 74/A, I-06123 Perugia (IT). **PICA, Monica** [IT/IT]; Fraz. Morano Madonnuccia 37/A, I-06123 Gualda Tadino (IT).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- (88) Date of publication of the international search report:
25 March 2004
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ION CONDUCTING COMPOSITE MEMBRANE MATERIALS CONTAINING AN OPTIONALLY MODIFIED ZIRCONIUM PHOSPHATE DISPERSED IN A POLYMERIC MATRIX, METHOD FOR PREPARATION OF THE MEMBRANE MATERIAL AND ITS USE

(57) Abstract: The invention provides composite membrane materials comprising a polymer of the state of art uniformly filled with a zirconium phosphate, preferably α -zirconium phosphate or zirconium phosphate sulfoarylenphosphonate particels. The composite membrane materials are preferably prepared starting from a solution of a polymer of the state of art and from a colloidal dispersion of α -zirconium phosphate or a zirconium phosphate sulfoarylenphosphonate. The colloidal particles are transferred into the solution of the polymer preferably by mixing the dispersion with the solution or by means of phase transfer. The membrane material is preferably obtained by removing the solvent by evaporation or by a suitable non-solvent. Besides the composite membrane materials and the preparation methods, the use of the above membrane materials is claimed as ionomeric membranes with high overall performance in high temperature, especially hydrogen, and in indirect methanol fuel cells and with decreased methanol crossover in direct methanol fuel cells.

WO 2003/077340 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/02550

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M8/10 H01M8/02 H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | WO 96 29752 A (GROT WALTHER GUSTAV ;RAJENDRAN GOVINDARAJULU (US); DU PONT (US)) 26 September 1996 (1996-09-26) cited in the application * see p.3, 1.4-19; p.10, 1.4-21; p.12, 1.9-31; p.20, 1.28-34 * the whole document | 1-23 |
| Y | CLEARFIELD A: "STRUCTURAL CONCEPTS IN INORGANIC PROTON CONDUCTORS" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 46, no. 1 / 2, 1 May 1991 (1991-05-01), pages 35-43, XP000243491 ISSN: 0167-2738 * see p. 38, left col. - p.40 * the whole document | 1-23 |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *8* document member of the same patent family

Date of the actual completion of the international search

20 October 2003

Date of mailing of the international search report

28/10/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Stellmach, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/02550

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| Y | SCHUTZ P ET AL: "MATERIALS FOR MEDIUM TEMPERATURE SOLID STATE FUEL CELLS" EXTENDED ABSTRACTS, ELECTROCHEMICAL SOCIETY. PRINCETON, NEW JERSEY, US, vol. 87-2, 18 October 1987 (1987-10-18), pages 248-249, XP000115049 ISSN: 0160-4619 the whole document | 1-23 |
| X | ALBERTI G ET AL: "Solid state protonic conductors, present main applications and future prospects" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 145, no. 1-4, 1 December 2001 (2001-12-01), pages 3-16, XP004310745 ISSN: 0167-2738 * see p.4,, table 1 * the whole document | 1-23 |
| Y | ALBERTI G ET AL: "ALL SOLID STATE HYDROGEN SENSORS BASED ON PELLICULAR A-ZIRCONIUM PHOSPHATE AS A PROTONIC CONDUCTOR" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 35, no. 1 / 2, 1 July 1989 (1989-07-01), pages 153-156, XP000132461 ISSN: 0167-2738 * see p.156, par. 4, conclusions * the whole document | 1-23 |
| Y | BONNET B ET AL: "HYBRID ORGANIC-INORGANIC MEMBRANES FOR A MEDIUM TEMPERATURE FUEL CELL" JOURNAL OF NEW MATERIALS FOR ELECTROCHEMICAL SYSTEMS, SN, MONTREAL, CA, vol. 3, no. 2, 2000, pages 87-92, XP000997606 ISSN: 1480-2422 * see p.87, left. col, * the whole document | 1-23 |
| Y | NORBY T: "Solid-state protonic conductors: principles, properties, progress and prospects" SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 125, 1999, pages 1-11, XP002252873 ISSN: 0167-2738 the whole document | 1-23 |

-/--

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/02550

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| Y | <p>EP 0 926 754 A (DE NORA SPA) 30 June 1999 (1999-06-30) cited in the application * see col. 3, l. 3 - col.4, l.21 and claim 1 * the whole document</p> | 1-23 |
| Y | <p>WO 01 54216 A (PELED EMANUEL ;AHARON ADI (IL); DUVDEVANI TAIR (IL); MELMAN AVI (I) 26 July 2001 (2001-07-26) * see p.3, l. 17-20, claims * the whole document</p> | 1-23 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/02550

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|--|--|
| WO 9629752 | A | 26-09-1996 | DE 69608793 D1 DE 69608793 T2 EP 0815606 A1 JP 2000516014 T WO 9629752 A1 US 5919583 A | 13-07-2000 01-02-2001 07-01-1998 28-11-2000 26-09-1996 06-07-1999 |
| EP 0926754 | A | 30-06-1999 | IT MI972733 A1 DE 69813752 D1 DK 926754 T3 EP 0926754 A1 JP 11250922 A US 6156184 A | 10-06-1999 28-05-2003 18-08-2003 30-06-1999 17-09-1999 05-12-2000 |
| WO 0154216 | A | 26-07-2001 | US 6447943 B1 US 6492047 B1 AU 2702101 A AU 2702201 A CA 2397536 A1 CA 2397568 A1 CN 1401143 T CN 1411618 T EP 1249052 A2 EP 1249053 A2 WO 0154220 A2 WO 0154216 A2 JP 2003520412 T JP 2003520413 T US 2003091883 A1 | 10-09-2002 10-12-2002 31-07-2001 31-07-2001 26-07-2001 26-07-2001 05-03-2003 16-04-2003 16-10-2002 16-10-2002 26-07-2001 26-07-2001 02-07-2003 02-07-2003 15-05-2003 |